

AD A 137484

(12)

REPORT No. ONR-2-6 (Interim)

PERIOD COVERED: 1 January 1983 through 31 December 1983

RESEARCH IN ENERGETIC COMPOUNDS

A Report on Work Sponsored by the
OFFICE OF NAVAL RESEARCH

Contract N00014-78-C-0147
NR 659-796/3-25-83

January 1984

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By

T. G. Archibald and K. Baum

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER. ONR-2-6	2. GOVT ACCESSION NO. AD-A137484	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Research in Energetic Compounds		5. TYPE OF REPORT & PERIOD COVERED Interim Summary 1 Jan 1983 - 31 Dec 1983
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Thomas G. Archibald and Kurt Baum		8. CONTRACT OR GRANT NUMBER(s) N00014-78-C-0147
9. PERFORMING ORGANIZATION NAME AND ADDRESS Fluorochem, Inc. 680 S. Ayon Ave. Azusa, CA 91702		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 659-796/3-25-83
11. CONTROLLING OFFICE NAME AND ADDRESS Department of the Navy Office of Naval Research, Code 432 Arlington, VA 22217		12. REPORT DATE January 1984
		13. NUMBER OF PAGES 38
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Reproduction in whole or in part is permitted for any purpose of the United States Government.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Nitroazetidines Nitroadamantanes Nitrations Nuclear magnetic resonance spectra Infrared spectra Chromatography		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) (over)		

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The synthesis of 1,3,3-trinitroazetidine was carried out by means of the reaction of 1-t-butyl-3-methanesulfonatoazetidine with sodium nitrite to give 1-t-butyl-3-nitroazetidine. Oxidative nitration gave 1-t-butyl-3,3-dinitroazetidine, and nitrolysis with acetyl nitrate gave 1,3,3-trinitroazetidine. Other routes were explored. 1-Benzhydryl-3,3-dinitroazetidine was obtained by nitrite displacement of 1-benzhydryl-3-methanesulfonatoazetidine, followed by oxidative nitration, but attempts to replace the benzhydryl group by nitrolysis, hydrogenation or bromination were unsuccessful. Nitration of 1-t-butyl-3-hydroxyazetidine, 3-methanesulfonatoazetidine, 3-carboxyazetidine and 3-hydroxyazetidine gave, respectively, 1-t-butyl-3-nitratoazetidine, 1-nitro-3-methanesulfonatoazetidine, 3-carboxy-1-nitroazetidine and 1-nitro-3-nitratoazetidine.

Bromination of 2,4-dioximinoadamantane under mildly acidic conditions gave 2,4-dibromo-2,4-dinitroadamantane. Reactions of 2-oximinoadamantane, 2,4-dioximinoadamantane and 2,6-dioximinobicyclo[3.3.1]nonane with neutralized hypochlorous acid resulted in replacement of the oxime groups with gem-dichloro groups. Oximes on cyclohexane rings, even with substituents to prevent ring inversions, gave the normal conversion to gem-chloronitroso groups. The sodium salt of 2-nitroadamantane reacted with tetranitromethane to give 2,2-dinitroadamantane, although the salt of nitrocyclohexane gave only the coupling product, 1,1-dinitrobicyclohexyl. In the presence of nitrite ion, the latter reaction gave 1,1-dinitrocyclohexane.

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I. INTRODUCTION

This report summarizes the research under Contract N00014-78-C-0147 during the period 1 January 1983 through 31 December 1983. The objective of this work is the synthesis of new high density, high energy compounds for explosives applications. Work was continued in the area of polynitroadamantanes. A new area of investigation is the synthesis of small ring energetic heterocycles.

II. AZETIDINE CHEMISTRY

A. DISCUSSION

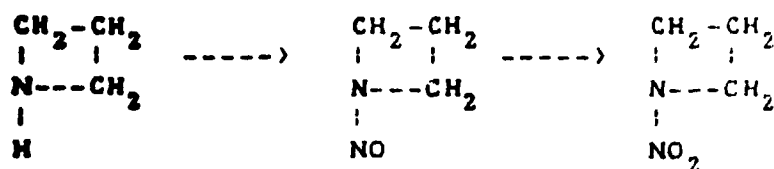
On the basis of its theoretical density and explosive properties, 1,3,3-trinitroazetidine was selected as a target compound. Calculations of the density and explosive properties, using the Miller and Chafin program, are shown in Table I. Previously on this program, research was aimed at the synthesis of nitrooxetanes for use as monomers,¹ and techniques that were developed for the introduction of gem-dinitro groups into the oxetane system provided potential applicability to the azetidine ring system.

TABLE I
Calculated Properties of 1,3,3-Trinitroazetidine

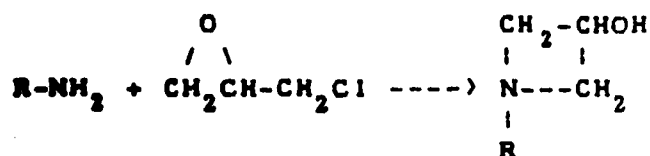
$\begin{array}{c} \text{CH}_2-\text{C}(\text{NO}_2)_2 \\ \quad \\ \text{N}---\text{CH}_2 \\ \\ \text{NO}_2 \end{array}$	Density.....	1.82
	Detonation velocity..	8.68 mm/microsec
	Detonation pressure..	353.54 kbar
	Heat of formation....	56.92 kcal/100 g
		109.35 kcal/mole

Although a considerable amount of work has been reported dealing with azetidines,² the only nitro-substituted example known is 1-nitro-

azetidine, which was synthesized from 1-nitrosoazetidine.³



N-Substituted azetidines with functional groups in the 3 position are readily accessible by the reaction of amines with epichlorohydrin.⁴

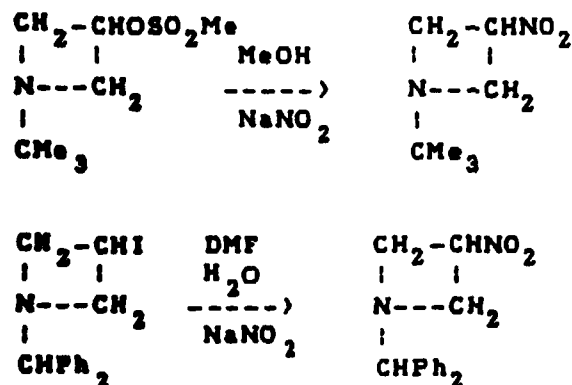


The benzhydryl groups of N-benzhydrylazetidine derivatives can be removed easily by catalytic hydrogenation⁵. On the other hand, N-t-butyl derivatives of larger-ring heterocycles are converted readily to nitramines by nitrolysis⁶. Thus N-t-butyl- and N-benzhydryl-3-hydroxyazetidine were chosen initially as starting materials for this work.

1-t-Butyl-3-hydroxyazetidine hydrochloride⁴ and 1-benzhydryl-3-hydroxyazetidine hydrochloride⁷ were obtained from the corresponding amines and epichlorohydrin. Reaction of these salts with methanesulfonyl chloride⁸ gave the corresponding 3-methanesulfonates.

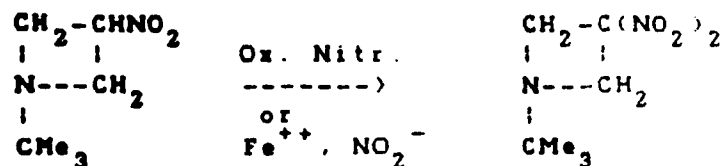
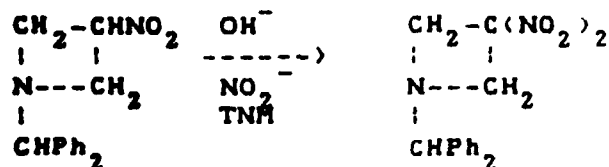
The direct displacement of these methanesulfonates by sodium nitrite was found to produce 3-nitroazetidine derivatives under rather limited conditions. The reaction of 1-t-butyl-3-methanesulfonatoazetidine with sodium nitrite and phlorguinol dihydrate in aqueous methanol at 0°C gave an 8% yield of 1-t-butyl-3-nitroazetidine in 48 h. This material was somewhat unstable, and reactions at higher temperatures or in more ionizing solvents such as DMF yielded no product. Because of the need to keep the reaction temperatures low, the less reactive 3-bromo or

3-tosylate derivatives failed to give the desired product. The benzhydryl derivative failed to give 1-benzhydryl-3-nitroazetidine under these conditions. This material was obtained in 11% yield from 1-benzhydryl-3-iodoazetidine and sodium nitrite in aqueous DMF at 50°C in the presence of phloroglucinol. The product was also obtained from iodoazetidine formed in-situ from the methanesulfonate and sodium iodide.

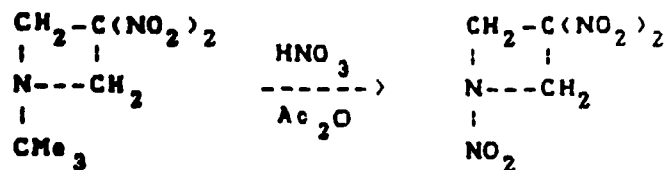


Nitrite displacements on four-membered rings have not been reported, and our attempts to prepare nitrooxetanes in this way were unsuccessful.⁹ The reactions apparently depend on the accelerating effect of the ring nitrogen.

1-Benzhydryl-3-nitroazetidine was converted to 1-benzhydryl-3,3-dinitroazetidine in 38% yield by reacting the nitronate salt with sodium nitrite and tetranitromethane in ethanol. Attempts to use the oxidative nitration reaction were unsuccessful because of low water solubility of the nitronate salt. On the other hand, 1-t-butyl-3-nitroazetidine was oxidatively nitrated with silver nitrate-sodium nitrite to give 1-t-butyl-3,3-dinitroazetidine in 39% yield. A 60% yield was obtained with a recently developed¹⁰ procedure in which the nitronate salt is reacted with sodium ferrocyanide, sodium persulfate and sodium nitrite. The tetranitromethane; or potassium ferrocyanate - sodium nitrite method gave only a 10% yield.



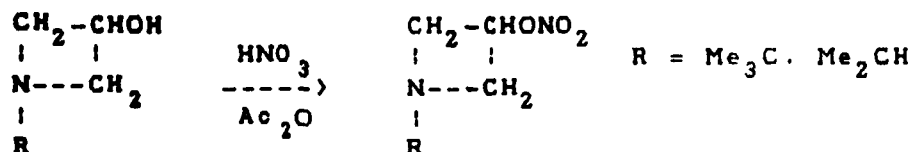
A number of attempts to convert the 1-benzhydryl-3,3-dinitroazetidine to 1,3,3-trinitroazetidine were made without success. The benzhydryl group is an efficient leaving group in hydrogenations, and the hydrogenation of 1-benzhydryl-3,3-dinitroazetidine was found to give an 80% yield of diphenylmethane. However, no nitro compounds were recovered. Direct nitration also failed to give 1,3,3-trinitroazetidine. 1-t-Butyl-3,3-dinitroazetidine was found to form stable salts with strong acids, and was thus resistant to nitrolysis even with hot mixed nitric and sulfuric acids. With 100% nitric acid, the nitrate salt was obtained, mp 155° (dec). The triflate salt and the hydrobromide were also isolated. Bromine formed a stable 1:1 adduct from which the starting material could be recovered. However, 1-t-butyl-3,3-dinitroazetidine reacted quickly with a mixture of nitric acid and acetic anhydride at ice bath temperature to give a 35% yield of the desired 1,3,3-trinitroazetidine.



1,3,3-Trinitroazetidine is a crystalline solid melting at 101°C

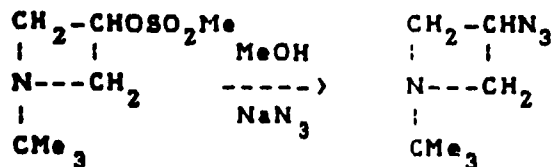
without decomposition. Above 150°C it underwent slow decomposition. Its density, determined by the flotation method, was found to be 1.83, and its crystallographic density, measured at the Naval Research Laboratory, was 1.84.

The electron-withdrawing effect of the gem-dinitro grouping appears to enable this nitrolysis to take place by destabilizing salts of the azetidine nitrogen. The reaction of 1-t-butyl-3-hydroxyazetidine with acetyl nitrate gave 1-t-butyl-3-nitratoazetidine, but no nitramine-containing product. Similarly, 1-i-propyl-3-hydroxyazetidine gave a high yield of 1-i-propyl-3-nitratoazetidine.



As an alternative route to 3-nitroazetidines, oxidation of the corresponding amines with m-chloroperbenzoic acid was tried. This reaction was used previously with the oxetane system.⁹ 1-t-Butyl-3-aminoazetidine, prepared from the tosylate and ammonia¹¹, was treated with m-chloroperbenzoic acid in refluxing ethylene chloride. No nitro compound was obtained.

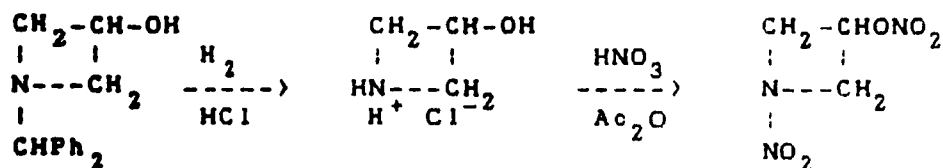
Work was initiated on a route using 1-t-butyl-3-azidoazetidine as an intermediate. This azide was obtained in 75% yield by reacting the tosylate with sodium azide in methanol.



Another method of introducing nitro groups into azetidines that was examined briefly is halogenation of the oximes. 1-t-Butyl-3-oximinoazetidine could not be prepared because of instability of the precursor, 1-t-butyl-3-azetidone. However, 1-benzhydryl-3-azetidone¹², obtained from the reaction of the alcohol with oxalyl chloride and dimethyl sulfoxide, was treated with hydroxylamine to give 1-benzhydryl-3-oximinoazetidine. The reaction of N-bromosuccinimide with this oxime cleaved of the benzhydryl group to form benzophenone but no evidence for nitro-containing products was obtained. Nitration of adamantanone oximes in refluxing methylene chloride gives gem-dinitro compounds¹. However, nitration of 1-benzhydryl-3-oximinoazetidine under these conditions gave only the starting ketone.

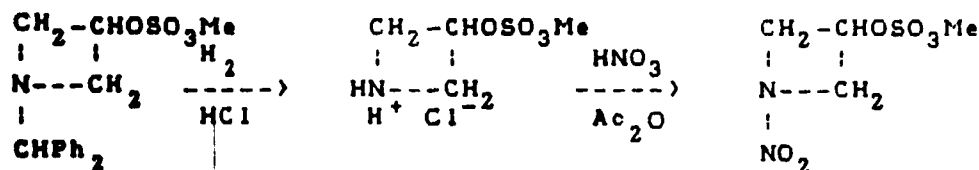
1-t-Butyl-3-cyanoazetidine¹³ was prepared, and was subjected to alkaline nitration conditions¹⁴, but the desired nitro derivative was not obtained. The nitrile also did not react with 100% nitric acid.

Another approach to nitroazetidines is to introduce the nitramino function before the C-nitro groups. Hydrogenation of 1-benzhydryl-3-hydroxyazetidine with Pearlman's catalyst⁵ gave a high yield of the hydrochloride of 3-hydroxyazetidine. Nitration of this salt with acetyl nitrate gave an 87% yield of 1-nitro-3-nitratoazetidine.



The nitrate ester is a solid melting at 70-71°C. with a density of 1.61. The material is available in good overall yield. Removal of the nitrate ester group did not take place readily, but exhaustive attempts were not made.

Hydrogenation of 1-benzhydryl-3-menthanesulfonatoazetidine similarly gave 3-menthansulfonatoazetidine, and nitration with acetyl nitrate gave a high yield of 1-nitro-3-methanesulfonatoazetidine. 1-Nitro-3-methanesulfonatoazetidine did not undergo displacement reactions with sodium nitrite or sodium azide. No reaction was observed below 100°C and the nitramine decomposed above that temperature



Nitration of 3-carboxyazetidine with acetyl nitrate gave 3-carboxy-1-nitroazetidine. This material was desired for conversion to an ester, followed by alkaline nitration. This approach was abandoned when attempted alkaline nitrations of the nitrile were unsuccessful.

B. EXPERIMENTAL

1-t-Butyl-3-hydroxyazetidine Hydrochloride. A modification of the procedure of Gaertner⁴ was used. A solution of 292 g (4 mol) of t-butylamine and 370 g (4 mol) of epichlorohydrin in 700 ml of hexane was stirred at room temperature for 3 days. The solvent was removed at 60°C under vacuum. 200 mL of acetonitrile was added, and the solution was refluxed for 4 h. Filtration, concentration of the filtrate and refiltration gave 445 g (67%) of 1-t-butyl-3-hydroxyazetidine hydrochloride, mp 165-167°C (lit⁴ 165-166°C).

1-Benzhydryl-3-hydroxyazetidine Hydrochloride This material was prepared by the procedure of Anderson and Lok⁷ using methanol as the

reaction solvent. An attempted preparation of 1-benzhydryl-3-azetidinol hydrochloride in hexane gave no crystalline products

1-t-Butyl-3-methanesulfonatoazetidine The method of Masuda, et al.¹¹ was used. Thus, a solution of 33 g (0.2 mol) of 1-t-butyl-3-hydroxyazetidine hydrochloride in 50 mL of water was made basic (pH 13) with 10% sodium hydroxide solution and was extracted with 3 75 to 100 mL portions of methylene chloride. The methylene chloride solution was dried over magnesium sulfate and the solvent was removed under vacuum. The unstable free amine was dissolved immediately in a solution of 30 g (0.3 mol) of triethylamine in 150 mL of dry benzene, and the solution was cooled to 0°C with an ice-salt bath. Methanesulfonyl chloride, 27.5 g (0.25 mol) was added dropwise at a rate to maintain the temperature below 4°C, and the solution was stirred for 2 hrs at 0° after the addition was complete. The precipitated triethylamine hydrochloride was filtered and was washed with 100 mL of benzene. Solvent was removed from the filtrates under vacuum at 45°C, and the residue, 40 g (70%) of 1-t-butyl-3-methanesulfonatoazetidine, was used without further purification.

1-t-Butyl-3-nitroazetidine A solution of 25 g (0.36 mol) sodium nitrite in 30 mL of water was added to a solution of 40 g (0.25 mol) of 1-t-butyl-3-methanesulfonyloxyazetidine and 32 g (0.2 mol) of phloroglucinol dihydrate in 300 mL of methanol, and the reaction mixture was allowed to stand at 0°C for 48 hrs. The resulting brown solution was stripped of solvent under vacuum at 30°C and 200 mL of water was added. This mixture, which decomposes on standing, was extracted rapidly with three 100 mL portions of methylene chloride. The methylene chloride solution was dried over magnesium sulfate and evaporated and the resultant oil was distilled to yield 2.5 g (8%) of 1-t-butyl-3-nitroazeti-

dine, bp 50-52°C (0.1 mm): IR (CH_2Cl_2) 3000 (C-H), 1550, 1430 cm^{-1} (NO_2); NMR (DCCl_3) δ 0.95 (s, 9 H, CH_3), 3.55 (asym d, J=3 Hz, 4 H, CH_2), 4.90 (quint, J=3 Hz, 1 H).

Anal. Calcd for $\text{C}_7\text{H}_{14}\text{N}_2\text{O}_2$: C, 53.14; H, 8.72; N, 17.70. Found: C, 52.87; H, 8.66; N, 16.33.

1-t-Butyl-3-nitroazetidine was stable at -15°C for long periods, but at room temperature in a sealed tube, it became brown and viscous in several days. Attempted preparations of this material starting with 1-t-butyl-3-bromoazetidine or 1-t-butyl-3-tosylatoazetidine or using other solvents such as DMF or using anhydrous conditions were unsuccessful. Longer reaction times up to one week failed to increase the yield and reactions at room temperature gave yields in the 3% range.

1-Benzhydryl-3-nitroazetidine. A solution of 31.5 g (0.1 mol) of 1-benzhydryl-3-methanesulfonatoazetidine, 7.5 g (0.11 mol) of sodium nitrite, 12 g of phloroglucinol dihydrate, 14 g (0.1 mol) of sodium iodide, and 20 mL of water in 200 mL of DMF was stirred at 50°C for 48 hrs and was then added to 150 mL of water. The mixture was extracted with 3 100 mL portions of ether to give 14.1 g of oil, shown by NMR analysis to be a 1:1 mixture of 1-benzhydryl-3-iodoazetidine and 1-benzhydryl-3-nitroazetidine. Column chromatography (silica gel, methylene chloride) to yield 3.0 g (11%) of 1-benzhydryl-3-nitroazetidine, mp 135-136°C: IR (CH_2Cl_2): 3050 (C-H), 1550, 1440 (NO_2), 1370, 1340, 1200, 1180, 1160, 1080, 1030 cm^{-1} ; NMR (CDCl_3) δ 3.5 (asym d, J=3 Hz, 4 H, CH_2), 4.3 (s, 1 H, CH), 4.8 (m, 1 H, CH), 7.0 (m, 10 H, Ar) ppm.

Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.31; H, 6.52; N, 10.10.

Similar results were obtained when 1-benzhydryl-3-iodoazetidine was

used in place of 1-benzhydryl-3-methanesulfonatoazetidine. Reactions using methanol as a solvent failed to produce the desired product. Reactions using lithium bromide in place of sodium iodide gave 1-benzhydryl-3-nitroazetidine in smaller yields. The use of anhydrous conditions and the addition of urea to dissolve the sodium nitrite in DMF did not improve the yield.

1-t-Butyl-3-bromoazetidine. A mixture of 29 g (0.1 mol) of 1-t-butyl-3-methanesulfonatoazetidine, 16 g (0.2 mol) of lithium bromide and 50 mL of acetone was stirred 24 h at room temperature. The salts were filtered, the acetone was evaporated on a rotary evaporator and the residual oil was distilled to yield 9.5 g (49%) of 1-t-butyl-3-bromoazetidine, bp 65-70°C (30 mm); IR (CH_2Cl_2): 3000, 2900 (C-H), 1480, 1360, 1220, 1100, 1090, 980 cm^{-1} ; NMR (CDCl_3) δ 1.0 (s, 9 H, CH_3), 3.4 (m, 4 H, CH_2), 4.2 (quint, 1 H,) ppm.

Anal. Calcd for $\text{C}_7\text{H}_{14}\text{NBr}$: C, 43.76; H, 7.34; N, 7.29. Found: C, 43.45; H, 7.04; N, 7.19.

1-Benzhydryl-3-iodoazetidine. A solution 22 g (0.66 mol) of 1-benzhydryl-3-methanesulfonatoazetidine and 12 g (0.8 mol) of sodium iodide in 100 mL of DMF was stirred at 60°C for 5 hrs and 200 mL of water was added. Extraction with 3 x 100 mL portions of ether gave a dark brown oil. This oil was dissolved in 30 mL of methylene chloride and was passed through 10 g of silica gel. Evaporation of the methylene chloride gave a waxy solid which was recrystallized from ethanol to give 14.3 g (70%) of 1-benzhydryl-3-iodoazetidine, mp 96-97°C; IR (CH_2Cl_2): 3050 (C-H), 1420, 1200, 1060, 1020 cm^{-1} ; NMR (CDCl_3) δ 3.6 (m, 4 H, CH_2), 4.2 (m, 1 H), 4.4 (s, 1 H), 7.0 (m, 10 H, Ar) ppm

Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{NI}$: C, 55.02; H, 4.62; N, 4.00. Found: C, 55.29; H, 4.80; N, 4.03.

1-Benzhydryl-3,3-dinitroazetidine. A solution of 1.0 g (0.0037 mol) of 1-benzhydryl-3-nitroazetidine and 0.30 g (0.0075 mol) of sodium hydroxide in 30 mL of ethanol was stirred for 30 min at room temperature and 1.0 g of sodium nitrite was added. Dropwise addition of 1.0 g (0.005 mol) of tetranitromethane resulted in an exothermic reaction, and a cool water bath was used to keep the temperature below 30°C. After 30 min, and the ethanol was evaporated on a rotary evaporator, and 50 mL of water was added and the aqueous layer was extracted twice with 50 mL of ether to give a waxy solid. Recrystallization from ethanol gave 0.44 g (38%) of 1-benzhydryl-3,3-dinitroazetidine, mp. 85-86°C; IR (CH_2Cl_2): 3050 (C-H), 1580, 1460 (NO_2), 1380, 1340, 1200, 900 cm^{-1} ; NMR (CDCl_3): δ 3.95 (s, 4 H, CH_2), 4.4 (s, 1 H, CH), 7.1 (m, 10 H, Ar) ppm.

Anal. Calcd for $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_4$: C, 61.33; H, 4.80; N, 13.42. Found: C, 61.34; H, 5.06; N, 13.23.

Attempted preparations of this material by oxidative nitration using silver nitrate - sodium nitrite or by using potassium ferrocyanide - sodium persulfate - sodium nitrite failed to give the desired product.

1-t-Butyl-3,3-dinitroazetidine. Freshly distilled 1-t-butyl-3-nitroazetidine (3.2 g, 0.0202 mol) was dissolved in a solution of 0.84 g (0.021 mol) of sodium hydroxide in 50 mL of water (30 min stirring at room temperature), and the solution was cooled to 10°C. Then a chilled solution of 4.9 g (0.1 mol) of sodium nitrite and 1.3 g (0.004 mol) of potassium ferrocyanide in 50 mL of water was added followed by 6.6 g (0.028 mol) of solid sodium persulfate. The temperature rose to 30°C after 10 min. The mixture was stirred for one h and then was extracted with methylene chloride (2 x 50 mL). The methylene chloride solution was dried with magnesium sulfate and the solvent was removed on a roto-

vac. The residual liquid was distilled to give 2.44 g (60%) of 1-t-butyl-3,3-dinitroazetidine, bp 70-72°C (0.2 mm), mp 17-18°C; IR (CH_2Cl_2): 3050 (C-H), 1580, 1465 (NO_2), 1375, 1320, 1240 cm^{-1} ; NMR (CDCl_3): δ 1.0 (s, 9 H, CH_3), 4.0 (s, 4 H, CH_2) ppm.

Anal. Calcd for $\text{C}_7\text{H}_{13}\text{N}_3\text{O}_4$: C, 41.38; H, 6.45; N, 20.68. Found: C, 41.66; H, 6.57; N, 20.11.

Oxidative nitration of 1-t-butyl-3-nitroazetidine to 1-t-butyl-3,3-dinitroazetidine was also accomplished using silver nitrate-sodium nitrite in 39% yield or tetranitromethane in 10% yield. This material was stable for long periods at room temperature and stable to 100% nitric acid, mixed nitric and sulfuric acids, and trifluoromethanesulfonic acid. It formed a nitrate salt, mp 155°C (dec).

Hydrogenation of 1-Benzhydryl-3,3-dinitroazetidine. A mixture of 0.40 g (0.0013 mol) of 1-benzhydryl-3,3-dinitroazetidine, 100 mL of methanol, 0.5 g of concentrated hydrochloric acid and 0.080 g of Pearlman's catalyst (5% palladium hydroxide on carbon) was hydrogenated at 50 psi at room temperature for 24 hours in a Parr bomb. At this time no further drop in pressure was observed and the catalyst was removed by filtration. Evaporation of the methanol and extraction of the residual oil with ether gave a small amount of ether insoluble oil that contained no nitro groups. The ether layer contained 0.17 g (80%) diphenylmethane, as identified by IR and NMR comparisons with authentic material.

1,3,3-Trinitroazetidine. Acetic anhydride (5 mL) was cooled with an ice bath to 2°C and 1.5 mL of 100% nitric acid was added dropwise. The mixture was stirred for 5 min and 0.75 g (0.0037 mol) of 1-t-butyl-3,3-dinitroazetidine was added dropwise. A waxy solid precipitated and slowly redissolved. After 1 hr. 50 mL of methylene chloride

was added, and the solution was washed with 50 mL of water and 50 ml of 10% sodium carbonate solution, dried with magnesium sulfate, and stripped of solvent. The residual solid was recrystallized three times from carbon tetrachloride to yield 0.25 g (35%) of 1,3,3-trinitroazetidine, mp 103-104°C; IR (CH_2Cl_2): 3050 (C-H), 1580, 1420 (NO_2) cm^{-1} ; NMR (CCl_4): δ 5.0 (s) ppm; density (AgNO_3 solution flotation) 1.83. This material decomposed above 150°C and a sample was detonated by a hammer blow.

Anal. Calcd for $\text{C}_3\text{H}_4\text{N}_4\text{O}_6$: C, 18.76; H, 2.10; N, 29.16. Found: C, 18.93; H, 2.16; N 26.81.

1-t-Butyl-3-nitratoazetidine. A solution of 5.0 g (0.038 mol) of 1-t-butyl-3-hydroxyazetidine in 10 mL glacial acetic acid was added dropwise at 10-15°C to a solution of acetyl nitrate prepared from 10 mL of 100% nitric acid and 20 mL of acetic anhydride. The mixture was kept at 10°C for 30 min and at 25°C for 5 hrs and then was poured over 100 mL of ice. The mixture was neutralized with 10% potassium hydroxide and was extracted twice with 50 mL of diethyl ether. The solution was dried over sodium sulfate and solvent was removed to yield 3.15 g (47%) of 1-t-butyl-3-nitratoazetidine as a liquid: IR (CH_2Cl_2): 3000 (C-H), 1610 (ONO_2), 1460, 1350, 1265, 1220, 1120 cm^{-1} ; NMR (neat) δ 0.95 (s, 9 H, CH_3), 3.2 (m, 4 H, CH_2), 5.2 (quint, 1 H, CH) ppm. This material decomposed on standing and was not subject to elemental analysis.

Similar reactions of 1-t-butyl-3-hydroxyazetidine with mixed nitric acid - sulfuric acid, or with 100% nitric acid lead only to formation of nitrate esters. No nitramines were observed.

1-i-Propyl-3-nitratoazetidine. A solution of 1 ml of concentrated sulfuric acid and 7 mL of 100% nitric acid was cooled to 5°C and 3.0 g

(0.02 mol) of 1-*i*-propyl-3-hydroxyazetidine hydrochloride, was added. The solution was stirred for 24 hrs at room temperature and was poured over 100 mL of ice. The water solution was neutralized with 10% aqueous potassium hydroxide and was extracted with 3 x 50 mL portions of methylene chloride. The methylene chloride solution was dried over magnesium sulfate and solvent was removed to yield 2.8 g (87%) of 1-*i*-propyl-3-nitratoazetidine: IR (CH_2Cl_2): 3000 (C-H) 1620 ($-\text{ONO}_2$), 1460, 1380, 1320, 1280, 1220, 1190, 1095 cm^{-1} . NMR (neat): δ 1.0 (d, J=3 Hz, 6 H, CH_3), 2.2 (m, 1 H, CHMe_2), 3.0 (m, 2 H), 3.6 (m, 2 H), 5.2 (m, 1 H, ring CH). This material formed a solid hydrochloride, mp 154°C (dec).

Anal. Calcd for $\text{C}_6\text{H}_{13}\text{N}_2\text{O}_3\text{Cl}$: C, 36.64; H, 6.66; N, 14.24. Found: C, 36.27; H, 6.67; N 14.05.

Similar reactions of 1-*i*-propyl-3-hydroxyazetidine with nitric acid or acetyl nitrate solutions gave nitrate esters but no nitramines.

1-*t*-Butyl-3-aminoazetidine. A solution of 29 g (0.1 mol) of 1-*t*-butyl-3-tosylatoazetidine in 100 mL of methanol saturated with ammonia was stirred for two days at room temperature. The solution was filtered and the methanol was removed under vacuum. The residual oil was dissolved in 100 mL of methylene chloride, washed with 50 ml of 10% sodium carbonate solution, dried with magnesium sulfate and stripped of solvent. Distillation of the resultant oil gave 5.0 (40%) of 1-*t*-butyl-3-aminoazetidine, bp 55-58°C (10 mm). Spectra and physical properties were identical to those reported.¹¹

Attempted Oxidation of 1-*t*-Butyl-3-aminoazetidine. A solution of 1.62 g (0.0012 mol) of 1-*t*-butyl-3-aminoazetidine in 5 ml of 1,2-dichloroethane was added dropwise to a refluxing solution of 5.5 g (0.03 mol) *m*-chloroparbenzoic acid in 50 mL of 1,2-dichloroethane. An exothermic reaction took place and a pale green solution was formed. The solution

was refluxed for 30 min, cooled, washed twice with 50 mL of pH 6.0 phosphate buffer. Removal of the solvent gave an oil that showed no IR nitro bands between 1500 and 1630 cm^{-1} . This oil was not investigated further.

1-t-Butyl-3-azidoazetidine. A solution of 14.0 g (0.049 mol) of 1-t-butyl-3-tosyloxyazetidine and 3.5 g of sodium azide in 50 mL of methanol was stirred at room temperature for 18 hrs. The methanol was evaporated and the residue was dissolved in 50 mL of methylene chloride and was washed with 50 mL of water and 50 mL of 10% sodium carbonate solution. The methylene chloride layer was dried over magnesium sulfate and solvent was removed to yield 5.7 g (0.037 mol, 75%) of crude 1-t-butyl-3-azetidine, a light brown oil essentially pure on the basis of NMR. An analytical sample was obtained by distillation (with difficulty because of foaming): bp 50-52 (0.5 mm); IR (CH_2Cl_2) 3000 (C-H), 2140 ($-\text{N}_3$), 1380, 1220, 1100, 1000 cm^{-1} ; NMR (CDCl_3) δ 0.95 (s, 9 H, CH_3), 3.0-4.0 (m, 5 H).

Anal. Calcd for $\text{C}_7\text{H}_{14}\text{N}_4$: C, 54.52; H, 9.15; N, 36.33. Found: C, 54.66; H, 9.50; N 36.18.

1-Benzhydryl-3-azetidine. A solution of 8.8 g (0.11 mol) of dimethyl sulfoxide in 20 mL of methylene chloride was added dropwise to a solution of 7.0 g (0.055 mol) of oxalyl chloride in 50 mL of methylene chloride at -78°C , and stirred for 10 min. Then a solution of 10 g (0.05 mol) of 1-Benzhydryl-3-hydroxyazetidine in 50 mL of methylene chloride was added dropwise and the mixture was stirred for 30 min. Then 22 g (0.11 mol) of triethylamine was added and the solution was warmed to room temperature. The methylene chloride solution was filtered, washed twice with 100 mL portions of water, dried over magnesium

sulfate and stripped of solvent to yield a dark oil. This oil was extracted with hot hexane (4 x 50 mL). Evaporation of the hexane gave 6.2 g (60%) of 1-benzhydryl-3-azetidone, mp 94-95°C (methanol), 70-71°C (ethanol), (lit.¹² 77-78).

1-Benzhydryl-3-azetidone was converted to 1-benzhydryl-3-oximinoazetidine with hydroxylamine hydrochloride and sodium carbonate in ethanol: mp 168-169°C (lit. 167-170°C).

Anal. Calcd for $C_{16}H_{16}N_2O$: C, 76.16; H, 6.39; N, 11.00. Found: C, 75.95; H, 6.28; N, 10.91.

Reaction of 1-Benzhydryl-3-oximinoazetidine with NBS. A solution of 2.5 g (0.01 mol) of 1-benzhydryl-3-oximinoazetidine in 100 mL of dioxane was added to a mixture of 6.0 g (0.03 mol) of n-bromosuccinimide, and 3.0 g of sodium bicarbonate in 50 mL of water. The reaction mixture became dark blue and then green over a 10 min period. After the mixture was stirred for 30 min, it was added to 300 mL of water and extracted three times with 100 mL portions of methylene chloride to give 1.2 g (67%) of benzophenone, identified by IR and NMR comparison with authentic material. The aqueous solution was made alkaline with 10% sodium hydroxide, and reextraction with methylene chloride gave only a trace of 1-benzhydryl-3-azetidone.

Nitration of 1-Benzhydryl-3-oximinoazetidine. To a solution of 1.0 g (0.004 mol) of 1-benzhydryl-3-oximinoazetidine in 10 mL of refluxing methylene chloride was added, dropwise, 1.5 mL of 100% nitric acid. The solution became dark green, blue and then colorless over a 10 min period. After 20 minutes, the solution was cooled and extracted twice with 10 mL of water, dried over magnesium sulfate and stripped of solvent. Extraction of the residue with 10 mL of chloroform yielded 0.10 g (10%) of unreacted starting material. Evaporation of the chloro-

form gave 0.80 g (77%) of 1-benzhydryl-3-azetidone,, identified by IR and NMR.

Attempted Preparation of 1-t-Butyl-3-cyano-3-nitroazetidine. A solution of 13.8 g (0.1 mol) of 1-t-butyl-3-cyanoazetidine¹³ and 17 g (0.15 mol) of potassium t-butoxide in 50 mL of tetrahydrofuran at -50°C and was stirred for 30 min and 11.6 g (0.11 mol) of propyl nitrate, was added dropwise. The solution was allowed to stand at room temperature for one hr and 100 mL of water was added. The mixture was extracted with ether to give starting 8.0 g (58 %) of recovered 1-t-butyl-3-cyanoazetidine, bp 70-72°C(4 mm). No nitro containing materials were observed.

Similar results were obtained when this reaction was attempted with 1-benzhydryl-3-cyanoazetidine.

Reaction of 1-t-Butyl-3-cyanoazetidine with Nitric Acid. A solution of 1.0 g (0.007 mol) 1-t-butyl-3-cyanoazetidine in 5 mL of 100% nitric acid was prepared at 5°C, and was stirred for 24 hrs at room temperature. The reaction mixture was quenched with 50 mL of water, and was made basic (pH >13) with 10% potassium hydroxide. The water was extracted with methylene chloride to give 0.80 g (80%) of recovered 1-t-butyl-3-cyanoazetidine. No nitramines were observed in the IR.

3-Nitrate-1-nitroazetidine. The addition 20 mL of 100% nitric acid to 100 mL of acetic anhydride, with ice bath cooling, was carried out at a rate such that the temperature did not exceed 15°C. After 30 min 10 g (0.1 mol) of 3-hydroxyazetidinium chloride was added at 10°C and the solution was stirred at room temperature for 6 hrs. The mixture was poured over 100 mL of ice and water. After the mixture was stirred for 20 min, the precipitate was filtered and recrystallized from chloroform

to give 16.3 g (87%) of 3-nitrato-1-nitroazetidine, mp 70-71°C, bp 115-118 (0.2 mm), density (AgNO₃ solution flotation) 1.61, IR (CH₂Cl₂): 3050 (C-H), 1640 (ONO₂), 1540, 1430 (NO₂), 1310, 1270, 1170, 1140, 1000, 840 cm⁻¹; NMR (CDCl₃): δ 4.5 (m, 4 H, CH₂), 5.3 (m, 1 H, CH) ppm.

Anal. Calcd for C₃H₅N₃O₅: C, 22.09; H, 3.09; N, 25.76. Found: C, 22.27; H, 3.06; N, 22.47.

3-Methanesulfonato-1-nitroazetidine. Nitric acid (108 mL, 100%) was added to 50 mL of acetic anhydride while the temperature was kept below 15°C, and the solution was stirred for 30 min. Then 5.6 g (0.03 mol) of 3-methanesulfonatoazetidinium chloride⁷ was added and the mixture was stirred at 15°C for 30 min. The solution was poured over 100 mL of ice and the mixture was stirred for 2 hrs. The solid which formed was filtered and recrystallized from ethanol and then chloroform to give 5.25 g (86%) of 3-methanesulfonato-1-nitroazetidine, mp 75-76°C; IR (CH₂Cl₂): 3050 (C-H), 1530 (NO₂), 1340, 1180, 1020, 960, 910 cm⁻¹; NMR (CDCl₃): δ 3.05 (s, 3 H, CH₃-S), 4.6 (m, 4 H, CH₂), 5.1 (m, 1 H) ppm.

Anal. Calcd for C₄H₈N₂O₅S: C, 24.36; H, 4.09; N, 14.20. Found: C, 24.50; H, 4.22; N, 14.09.

Reaction of 3-Methanesulfonato-1-nitroazetidine with Sodium Nitrite. A solution of 1.8 g (0.01 mol) of 3-methanesulfonato-1-nitroazetidine, 0.8 g (0.011 mol) of sodium nitrite, 1.4 g of phloroglucinol, 0.2 g of urea, and 0.5 g of lithium bromide in 40 mL of DMF was stirred at room temperature for 4 days. NMR analysis showed no reaction, and heating the solution 2 days at 40°C gave 1.55 g (86 %) of recovered 3-methanesulfonato-1-nitroazetidine.

Reaction of 3-Methanesulfonato-1-nitroazetidine with Sodium Azide
A solution of 1.8 g (0.01 mol) of 3-methanesulfonato-1-nitroazetidine and 1.0 g (0.015 mol) of sodium azide in 30 mL of diethyleneglycol was

stirred at 80°C for 24 hrs. NMR and IR analysis of showed no reaction. Heating the mixture to 130°C gave an intractable tar.

3-Carboxy-1-nitroazetidine. To a cooled solution of 50 mL of acetic anhydride was added 10 mL of 100% nitric acid, with the temperature maintained below 15°C. This solution was stirred for 10 min and 5.0 g (0.036 mol) of 3-carboxyazetidinium chloride⁷ was added. After 10 min, an exothermic reaction occurred and the solid dissolved. The solution was stirred for 8 hrs and was then poured over 100 mL of ice. The mixture was extracted twice with 100 mL portions of methylene chloride, and the aqueous layer concentrated to 25 mL and extracted twice with 50 mL of ether. Evaporation of the ether and trituration of the residual oil with methylene chloride gave a solid which was recrystallized from ether to give 3.4 g (65%) of 3-carboxy-1-nitroazetidine, mp 132-134°C. IR (KBr): 3100-2900 (O-H), 1695 (C=O), 1540, 1430 (NO₂), 1300, 1220, 1160, 920 cm⁻¹. NMR (D₂O): δ 3.5 (m, 1 H), 4.5 (assym d, J = 3 Hz, 4 H). Anal. Calcd for C₄H₆N₂O₄: C, 32.88; H, 4.14; N, 19.17. Found: C, 32.85; H, 4.86; N 18.98.

III. ADAMANTANE CHEMISTRY

A. DISCUSSION

A study of the synthesis of carbocyclic polynitro compounds was initiated in the preceding year¹ with the objective of producing useful high density explosives. With monofunctional adamantanes as model compounds, intermediates to geminal dinitro groups were obtained by several routes: direct nitration of oximes, bromination or chlorination to halonitro compounds, and oxidation of oximes or amines to nitro compounds. Extension of this work provided 2,2,6,6-tetranitroadamantane. To obtain more energetic adamantanes based on gem-dinitro substituents, it is necessary to operate on 2,4 substituents. The principal objective has been to develop a route to 2,2,4,4-adamantane, and model studies toward this end were continued with simple adamantanes and with structurally related bicyclononanes. Geometrical crowding of nitro groups is an apparent obstacle.

The direct nitration of 2,4-dioximinoadamantane gave an internal dinitro-nitroso dimer¹ and no tetranitro compound, suggesting that because of steric requirements the nitroso intermediate dimerizes before it is able to further oxidize. Attempts to brominate this oxime under normal conditions were unsuccessful. A recent paper on the chlorination of oximes¹⁵ suggested that halogen reactions of oximes might be pH dependent. Therefore, the reaction of N-bromosuccinimide with 2,4-dioximinoadamantane was carried out under mildly acidic conditions and at subambient temperatures, and 2,4-dibromo-2,4-dinitroadamantane was isolated in 5% yield. The material, a mixture of isomers, was characterized spectrally and by elemental analysis. Its melting point is 150-

170°C. The fact that this material with bulky groups in the 2,4-positions is stable gives encouragement that the 2,2,4,4-tetranitroadamantane structure is attainable.

The reduction of 2,4-dibromo-2,4-dinitroadamantane to 2,4-dinitroadamantane is under study. Sodium borohydride gave a complex mixture of products, and other reagents are being examined.

Attempts to prepare 2,4-dinitroadamantane from the dioxime by direct oxidation with pertrifluoroacetic acid were not successful. Adamantane oximes are known to undergo facile rearrangement to ring expanded asa-homoadamantanes. This occurred in the peracid oxidations, even in buffered acetonitrile solutions, and no nitro compounds were obtained.

The halogenation of oximes under alkaline conditions usually leads to ketone formation. An exception is the reaction of 2-oximinoadamantane which forms 2-chloro-2-nitroadamantane¹ without an added oxidizing agent. The normal method to convert oximes to chloronitro compounds involves the direct reaction with chlorine gas to form a chloronitroso derivative which can be oxidized with ozone or peracid to the chloronitro compound. Corey¹⁵ found that oximes react with aqueous hypochlorous acid at pH 5.5 to give gem-chloronitroso compounds, which are subsequently oxidized to gem-chloronitro compounds in benzene with alkaline hypochlorite in the presence of a phase transfer agent such as tetra-n-butylammonium hydrogen sulfate. In our hands, this reaction gave yields in excess of 90% with simple oximes and even with norbornyl structures.

In the adamantane system, however, the reaction of oximes with pH 5.5 hypochlorous acid gave an anomalous chlorination reaction. The reaction of 2-oximinoadamantane gave a 59% yield of 2,2-dichloroadamanta-

tane, a 37% yield of 2-chloro-2-nitroadamantane and a 4% yield of adamantanone. The reaction of 2,6-dioximinobicyclo[3.3.1]nonane yielded 60% of 2,2,6,6-tetrachloro-bicyclo[3.3.1]nonane and no nitro compounds were detected. The same product would be expected from the reaction of bicyclo[3.3.1]nonane-2,6-dione with phosphorus pentachloride, but instead a material was obtained that appears, on the basis of analytical data, to be 2,6,6-trichloro-2-oxatricyclo[3.3.1^{2,7}]decane. The same material was obtained from the reaction of 2,2,6,6-tetrachloro-bicyclo-[3.3.1]nonane with base. The reaction of 2,4-dioximinoadamantane with hypochlorous acid gave 2,2,4,4-tetrachloroadamantane and no dichloro dinitro derivative. The anomalous reaction cannot be explained simply on the basis of the inflexibility of the adamantane ring structure. *t*-Butyl groups are known to prevent *cis-trans* conversions of cyclohexane rings, and 4-*t*-butyloximinocyclohexane and 2-*t*-butyloximinocyclohexane both underwent normal reactions to give the chloronitroso derivatives.

Differences were also observed between adamantane systems and cyclohexanes in conversions of nitronate salts to gem-dinitro compounds. For example, the sodium salt of 2-nitroadamantane was converted to 2,2-dinitroadamantane with tetranitromethane in high yield. On the other hand, the sodium salt of nitrocyclohexane reacted with tetranitromethane to give exclusively the coupling product, 1,1'-dinitrobicyclohexyl. In the presence of sodium nitrite, however, this reaction gave a 24% yield of the coupling product and a 76% yield of 1,1-dinitrocyclohexane. The reaction thus has similarities to the oxidative nitration, with tetranitromethane functioning as an electron transfer reagent. The differences between adamantanes and cyclohexanes are not readily explainable.

B. EXPERIMENTAL.

2,2,6,6-Tetrachloro-bicyclo[3.3.1]nonane. A pH meter was used to neutralize 200 mL of commercial pool bleach (5% sodium hypochlorite) to pH 3.5 at 0-5°C with 10% sulfuric acid. Then 100 mL of benzene and 5.0 g (0.027 mol) of solid bicyclo[3.3.1]nona-2,6-dione dioxime were added rapidly with stirring. As the dioxime dissolved, the solution became deep blue. After 1 h, the benzene layer was removed and stirred with 100 mL of unneutralized bleach and 0.5 g of tetra-n-butylammonium bisulfate for an additional 2 h. The solution became colorless. The organic layer was washed with 50 mL of water and dried over magnesium sulfate. Removal of the solvent and distillation yielded 4.2 g (60%) of 2,2,6,6-tetrachloro-bicyclo[3.3.1]nonane, bp 112-115 (0.3 mm), mp 20-22°C; IR (CH_2Cl_2) 3000 (C-H), 1460, 1440 (C-Cl) cm^{-1} ; NMR (CDCl_3) δ 2.0-2.8 ppm.

Anal. Calcd for $\text{C}_9\text{H}_{12}\text{Cl}_4$: C, 41.26; H, 4.58; Cl, 54.14. Found: C, 41.19; H, 4.32; Cl, 54.52.

2,6,6-Trichloro-2-oxatricyclo[3.3.1^{2,7}]decane. Phosphorus pentachloride (10 g, 0.05 mol) was added with stirring to a solution of 3.0 g (0.02 mol) of bicyclo[3.3.1]nona-2,6-dione in 50 mL of methylene chloride. After 15 min, the organic layer was washed (2 x 100 mL of water), dried over magnesium sulfate and stripped of solvent to yield 6.1 g of crude oil. Distillation gave 3.1 g (68%) of 2,6,6-trichloro-2-oxatricyclo[3.3.1^{2,7}]decane, bp 86-88°C (0.3 mm); IR (CH_2Cl_2) 3000 (C-H), 1440 (C-Cl), 1300, 1100, 1000, 920 cm^{-1} ; NMR (CDCl_3) δ 1.8-2.8 (m, 10 H), 5.6 (m, 1 H) ppm.

Anal. Calcd for $\text{C}_9\text{H}_{11}\text{Cl}_3\text{O}$: C, 44.75; H, 4.59; Cl, 44.03. Found: C, 44.44; H, 4.57; Cl, 44.01.

G.l.c. analysis of the crude reaction mixture on a 4' 3% SE-30 column at 150°C failed to show the presence of any 2,2,6,6-tetrachloro-

bicyclo[3.3.1]nonane.

Reaction of 2,2,6,6-Tetrachloro-bicyclo[3.3.1]nonane with Base. A solution of 0.1 g (0.0004 mol) of 2,2,6,6-tetrachloro-bicyclo[3.3.1]nonane in 5 mL of tetrahydrofuran was stirred for 2 weeks with 0.1 g of potassium *t*-butoxide. Then the solvent was removed and the residual oil was dissolved in 50 mL of methylene chloride, washed with 50 mL of water, dried with magnesium sulfate and stripped of solvent to give 0.05 g of an oil identified by nmr and g.l.c. as 2,6,6-trichloro-2-oxabicyclo[3.3.1]^{2,7}decane. G.l.c. analysis did not detect either starting 2,2,6,6-tetrachloro-bicyclo[3.3.1]nonane or bicyclo[3.3.1]nona-2,6-diene.

No reaction took place between 2,2,6,6-tetrachloro-bicyclo[3.3.1]nonane and sodium acetate in refluxing acetic acid (48 h) or potassium hydroxide in ethanol (48 h at 25 °C).

Reaction of 2-Oximinoadamantane with Hypochlorous Acid. A mixture of 50 mL of commercial pool bleach (5% sodium hypochlorite) and 50 mL of ice was acidified to pH 5.5 with phosphoric acid using a pH meter. Then, 1.0 g (0.04 mol) of 2-oximinoadamantane suspended in 20 mL of benzene was stirred with the bleach solution for 10 min at 20-25 °C. The solid became blue, dissolved and decolorized. The organic layer was separated, washed with water, dried over magnesium sulfate and evaporated to yield 0.75 g of an oil. Quantitative g.l.c. analysis of this oil showed it to contain 4% 2-adamantanone, 59% 2,2-dichloroadamantane and 37% 2-chloro-2-nitroadamantane. The 2,2-dichloroadamantane was identified by comparison with an authentic sample.¹⁶

Reaction of 2,4-Dioximinoadamantane with Hypochlorous Acid. A solution of 100 mL pH 5.5 aqueous bleach was neutralized with phosphoric

acid as described above and 2.0 g (0.01 mol) of 2,4-dioximinoadamantane suspended in 100 mL of benzene was added. The solid became blue, dissolved and rapidly decolorized. After 1 h, the organic layer was washed with 100 mL of water, dried over magnesium sulfate and stripped of solvent to yield 1.8 g of an oil. Column chromatography (silica gel, with 9:1 hexane-acetone) gave 0.35 g (13%) of 2,2,4,4-tetrachloroadamantane, mp 195°C (sealed tube, subl) 110°C, 1 atm; IR (CH_2Cl_2) 3000 (C-H), 1450 (C-Cl), 1240, 1080, 1040, 1000, 900, 840, 820 cm^{-1} ; NMR (CDCl_3) δ 1.7 (2 H), 2.3 (4 H), 2.6 (4 H), 2.85 (2 H) ppm.

Anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{Cl}_4$: C, 43.8; H, 4.73. Found: C, 43.79; H, 4.52.

Reaction of Cyclic Oximes with Hypochlorous Acid. A solution of 10.0 g (0.059 mol) of 4-t-butyl-1-oximinocyclohexane in 50 mL of benzene and 0.5 g of tetra-n-butyl ammonium hydrogen sulfate were stirred with 100 mL of neutralized commercial 5% pool bleach (adjusted to pH 5.5 with 20 g of disodium hydrogen phosphate and phosphoric acid). The solution turned blue immediately and decolorized after 10 min. The organic layer was separated and dried over magnesium sulfate. G.l.c. analysis (120°C, 4' SE-30 column) showed only one material. The crude material, 10.0 g (92%), was distilled to yield 8.4 g (78%) of 4-t-butyl-1-chloro-1-nitrocyclohexane, bp 96-98°C (0.2 mm) (reported¹⁵ yield 82%).

As a reference, 1.0 g (0.0055 mol) of 4-t-butylcyclohexanone was reacted with 2.0 g of phosphorus pentachloride in 30 mL of methylene chloride for 2 hours at 25°C. The organic layer was washed with 100 mL of water and dried over magnesium sulfate. G.l.c. analysis showed two peaks in relative area ratios of 35:65 at shorter retention times than that of 4-t-butyl-1-chloro-1-nitrocyclohexane. NMR analysis suggests these materials are 4-t-butyl-1,1-dichlorocyclohexane and 4-t-butyl-1-

chlorocyclohexene. Neither of these materials were observed in the chromatogram of crude 4-*t*-butyl-1-chloro-1-nitrocyclohexane

Similarly, 1-oximinocyclohexane, 2-*t*-butyl-1-oximinocyclohexane, and oximino-*d*-camphor gave the reported chloro nitro derivatives¹⁵ without detectable amounts of gem-dichloro derivative

Peroxytrifluoroacetic Acid Oxidation of 2-Oximinoadamantane A mixture of 25 g of disodium hydrogen phosphate, 21 g (0.1 mol) of trifluoroacetic anhydride, and 50 mL of acetonitrile was treated dropwise with 1.8 g of 50% hydrogen peroxide at 10-15°C. After 30 min, 1.6 g (0.01 mol) of 2-oximinoadamantane in 50 mL of acetonitrile was added dropwise with rapid stirring at the reflux temperature. A transient blue color appeared. After 1 h the solvent was evaporated, and the residual oil was diluted with 50 mL of methylene chloride and was washed with 200 mL of water. The organic layer was dried over magnesium sulfate and solvent was removed to give 1.4 g (87%) of 3-oxahomoadamantan-2-one, identified by IR and NMR comparisons to authentic material.¹⁸

2,4-Dibromo-2,4-dinitroadamantane. A mixture of 27 g (0.15 mol) of *n*-bromosuccinimide and 15 g of sodium bicarbonate in 150 mL of 20:80 *o*-dioxane-water was cooled to 10°C and 5.0 g (0.025 mol) of 2,4-dioximinoadamantane was added. The solid became green and slowly dissolved. The mixture was stirred 48 h and was extracted with methylene chloride (4 x 100 mL). The organic layer was washed with 100 mL of water, dried with magnesium sulfate and solvent was evaporated to give 3.1 g of crude oil. Column chromatography (silica gel, 95:5 hexane-acetone) gave 0.52 g (5%) of 2,4-dibromo-2,4-dinitroadamantane, (mixture of isomers), mp 150-170; IR (CH_2Cl_2), 3000 (C-H), 1560, 1420 (NO_2), 1220 cm^{-1} ; NMR (CDCl_3) δ 2.0-3.0 (11 H), 3.95 (1 H) ppm.

Anal. Calcd for $C_{10}H_{12}Br_2N_2O_4$: C, 31.27; H 3.37; N 7.29. Found: C, 31.23; H, 3.33; N, 7.25.

Reduction of 2,4-Dibromo-2,4-dinitroadamantane with sodium borohydride in methanol gave a complex mixture of nitro- and carbonyl-containing materials.

Reaction of Nitrocyclohexane with Tetranitromethane. A solution of 4.0 g (0.03 mol) of nitrocyclohexane in 10 mL of ethanol was stirred with 1.3 g (0.033 mol) of sodium hydroxide in 5 mL of water for 30 min. Then, 4.0 g (0.03 mol) of tetranitromethane was added dropwise and the solution was stirred for 1 h. The ethanol was evaporated and the residual oil was dissolved in 50 mL of methylene chloride and was washed with water (3 x 100 mL). The organic layer was dried over magnesium sulfate and stripped of solvent to yield 3.75 g (92%) of 1,1'-dinitrobicyclohexyl, mp 222°Cdec , (lit $217-221^{\circ}\text{C}$). In another experiment, 2.0 g (0.015 mol) of nitrocyclohexane and 0.6 g (0.015 mol) of sodium hydroxide, were stirred with a solution of 3.5 g (0.05 mol) of sodium nitrite in 15 mL of water for 30 min, and 3.0 g (0.015 mol) of tetranitromethane was added dropwise. The reaction mixture was worked up as above to yield 0.90 g of a waxy solid. NMR analysis of the product showed 24% 1,1'-dinitrobicyclohexyl and 76% of 2,2-dinitrocyclohexane (6% and 26% conversions respectively).

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